Quarterly Report No. 6
PHYSICAL AND RHEOLOGICAL PROPERTIES OF
NITROSO RUBBERS
25 September through 24 December 1964

Contract Nr. DA19-129-AMC-151(N)
(O.I. 9115)

14 January 1965

MONSANTO RESEARCH CORPORATION
A SUBSIDIARY OF MONSANTO COMPANY

DAYTON
LABORATORY

DAYTON, OHIO 45407

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MRC Project No. 4013(4505)
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For

U. S. Army Natick Laboratories
Natick, Massachusetts

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ABSTRACT

Four nitroso gum samples produced by Thiokol Chemical Corporation and supplied by the U. S. Army, Natick, Massachusetts, were characterized by IR, NMR, elemental analysis, intrinsic viscosity, X-ray diffraction, TGA, DTA and Clash-Berg shear modulus. Infrared analyses indicated that the four gums were basically similar. NMR confirmed a previously reported structure of

$$\left[\begin{array}{l} N \\ | \\ CF_3 \end{array}-CF_2CF_2-O\right]_x$$

Elemental analysis, however, indicated a variation in fluorine content from 61 to 67%. Molecular weights by intrinsic viscosity were in the range of 1.0 to 1.3 x 10^6. TGA confirmed a previously disclosed weight loss at 75°C with unzipping at 260°C. DTA exhibited a mild exotherm at 250°C. with an EXPLOSIVE exotherm at 295°C. Glass transitions of -60°C and -45°C were found by means of the Clash-Berg shear modulus apparatus. However, it was felt that the -60°C transition may be due in part to the presence of solvent.

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I. INTRODUCTION

The fluorinated nitroso rubber to be characterized in this program is considered to be a highly solvent-resistant, stable, low and high temperature rubber. The degree of its worth in these respects can only be determined through a characterization of its basic physical properties. The purpose of the characterization is to describe the rubber for its use and further improvement or modification.

Six nitroso gum samples, listed as ZR-561-XP5675, XP5702, XP5812, XP5887, XP5806, and XP5704, produced by the Thiokol Chemical Company, were delivered to Monsanto Research Corporation via the Natick Laboraties for characterization.

Four of the nitroso gum samples were characterized using infrared spectroscopy, nuclear magnetic (F^{19}) resonance, elemental analysis, intrinsic viscosity, X-ray diffraction, thermogravimetric analysis, differential thermal analysis, and Clash-Berg shear modulus.

II. RESULTS

Four samples of nitroso gum stock (ZR-561-XP5675, XP5702, XP5812, and XP5887) which were of adequate quantity to justify initial characterization received the following analysis.

A. INFRARED SPECTROSCOPY

The infrared spectra for the four ZR-561 gum samples - XP5675, XP5702, XP5812 and XP5887 - were basically similar to the spectrum found for the 3M gum previously tested (Ref. 1). Several minor differences between the samples were noted, however. Sample XP5675, Figure 1, did not exhibit the weak-to-medium absorptions at 2530, 2400, 2085 and 2010 cm^{-1} shown by the other samples. These absorptions appear to be overtones (first harmonics) of the C-O-N stretching absorptions at 1103 and 1065 cm^{-1} and the C-F stretching absorptions seen at 1300, 1245 and 1153 cm^{-1}. However, the conspicuous absence of these weak-to-medium bands has not been explained. They are customarily seen in spectra of perfluorocarbons.

Inasmuch as practically no infrared frequency assignments were found for the perfluorocarbons in standard sources, only tentative conclusions may be drawn at this time. The peak at 830 cm^{-1} is believed due to $-CF_2-CF_2-$ bend, and that at 745 cm^{-1} either to $-CF_2-CF\langle$ or $\rangle CF-CF\langle$, neither of which appears in the idealized average structure obtained by NMR. Significantly, no $-CF(CH_3)_2$, which would appear at 730 cm^{-1}, was seen in any of the spectra, nor was $-CF_2CF_3$ seen, which would appear at 735 cm^{-1}. Figures 2, 3 and 4 show the spectra for samples XP5702, XP5812 and XP5887, respectively. Sample XP5702 exhibits a spurious peak at 1735 cm^{-1} in the region normally assigned to saturated nonfluorinated esters and aldehydes, α-halogen ketones and α-halogen acids. The most likely explanation, considering the slight brownish color of the sample, is that overtemperature at some point in the processing allowed some trace oxidation or rearrangement to halogenated ketones and acids.

B. NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Shown in Figure 5 is the NMR spectrum obtained for sample XP5675. The spectra for the remaining samples were almost identical, although small deviations were noted in exact peak location and height. Listed in Table 1 are these peaks and their assignments. The structure defined is:

$$\left[\begin{array}{l} N-CF_2CF_2-O \\ | \\ CF_3 \end{array}\right]_x,$$

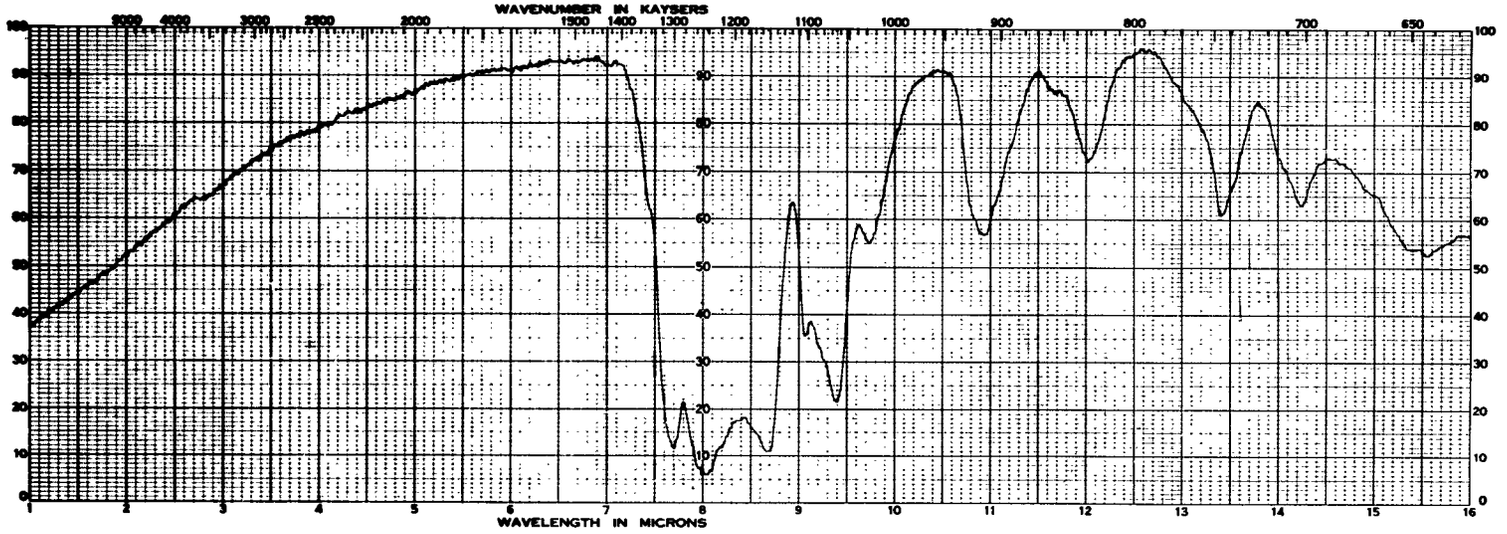


Figure 1. Infrared spectrum of nitroso rubber sample XP-5675

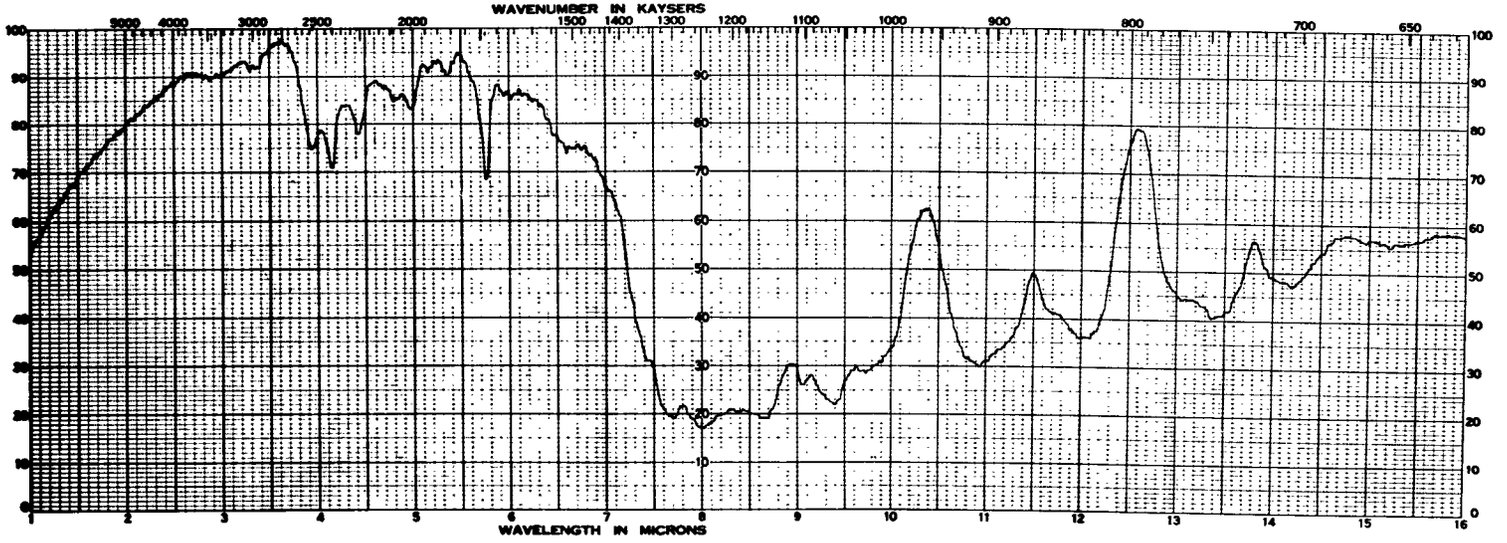


Figure 2. Infrared spectrum of nitroso rubber sample XP-5702

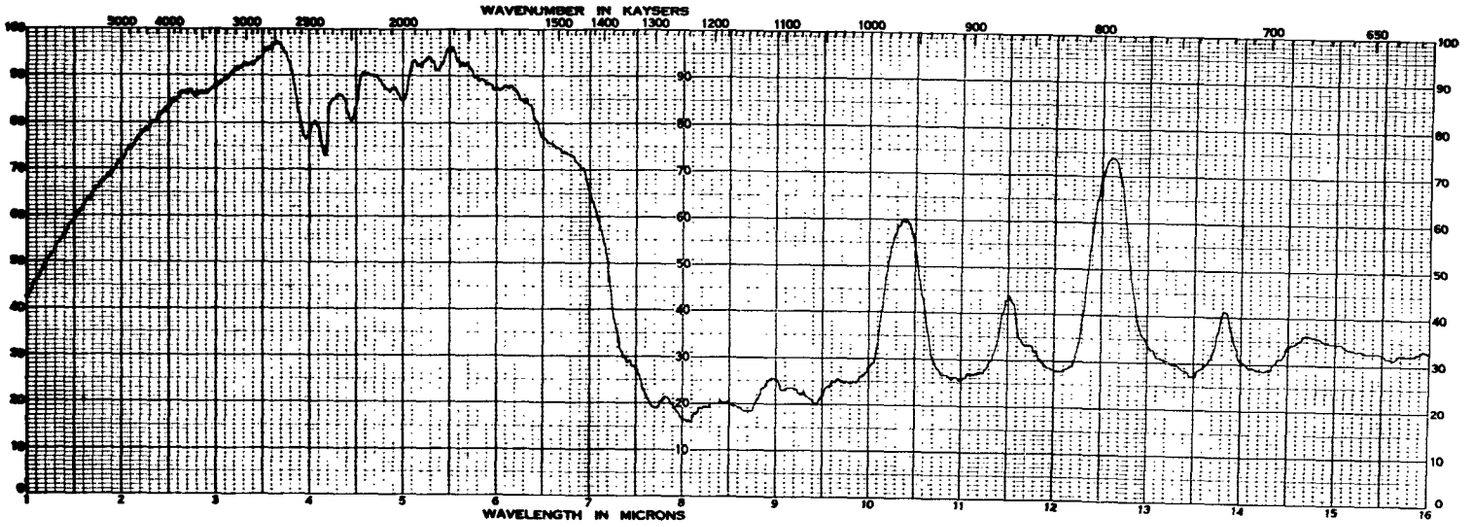


Figure 3. Infrared spectrum of nitroso rubber sample XP-5812

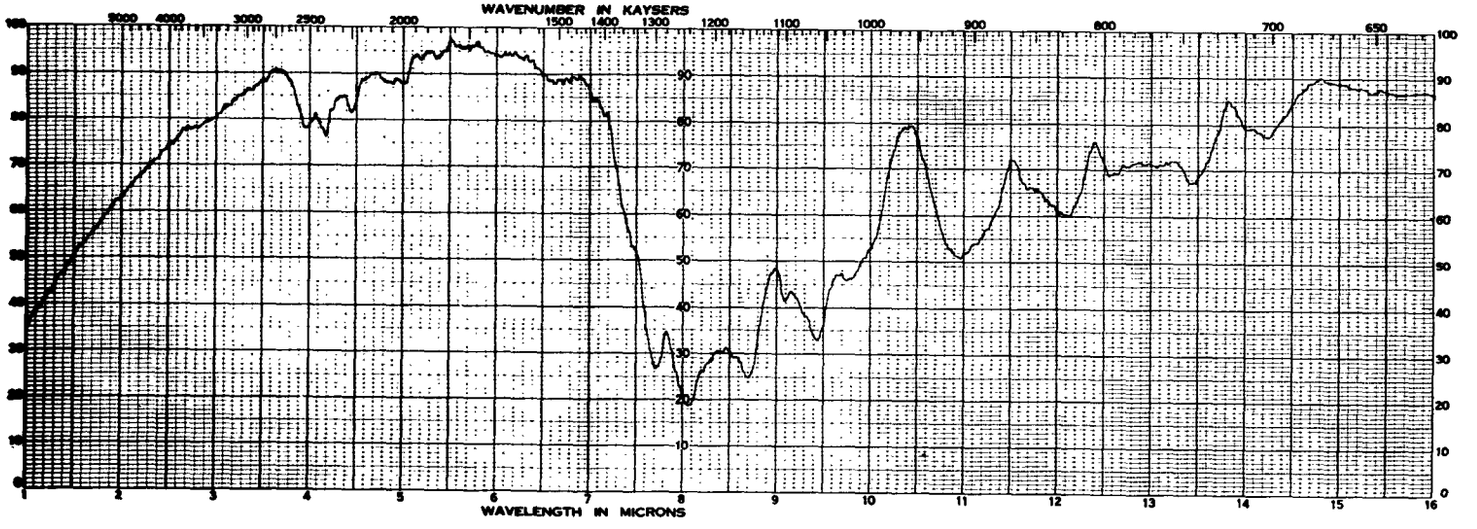


Figure 4. Infrared spectrum of nitroso rubber sample XP-5887

RF Frequency 40.0 Mc

Nuclei F^{19}

Sample No. ZR-561

MONSANTO RESEARCH CORPORATION

Nuclear Magnetic Resonance File Card

File No. _____

Request No. 3619

Description and/or Formula NITROSO RUBBER ZR-561

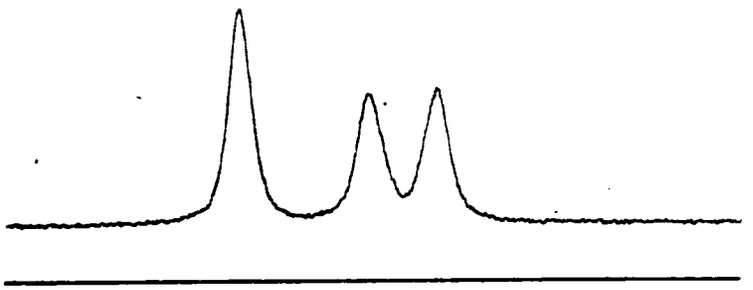
Date Run: 12/21/64

Submitter H. Wilson Job. No. 4505 Operator JES

Peak		1		2	3			
PPM		-11.5		+11.5	+24.0			
Area Ratio		3.0		2.0	2.0			

Reference: Trifluoroacetic Acid
Resolution: H-SH

INST. DATA:
RF Gain 4
RF Field 3 C 1 F
RF Current 10 uA
Sw. Freq.: C F
Sw. Field: C F
Attenuation X
Chart Speed 2 mm/Sec.
Probe Insert 5 mm
Spin Tube 5 mm
Sweep Rate: Fast 100



Peak								
PPM								
Area Ratio								

Reference: _____
Resolution: H-SH

INST. DATA:
RF Gain _____
RF Field C F
RF Current uA
Sw. Freq.: C F
Sw. Field: C F
Attenuation X
Chart Speed mm/Sec.
Probe Insert mm
Spin Tube mm
Sweep Rate: _____

Figure 5. F^{19} resonance spectrum of nitroso rubber sample

Table 1

NMR SPECTROSCOPY[a] OF NITROSO RUBBERS

Sample Number	Chemical Shift of[b] Peaks, ppm			Area Ratio of Peaks		
	1	2	3	1	2	3
XP5675	-11.4	+11.5	+24.0	3.0	1.9	2.0
XP5702	-11.4	+11.7	+24.2	3.0	2.0	1.9
XP5812	-11.3	+11.7	+24.3	3.0	1.9	2.0
XP5887	-11.5	+11.5	+24.0	3.0	2.0	1.9
Assignments				$-N(CF_3)$	$-N(CF_2)CF_2$	$-O(CF_2)CF_2$

[a] F^{19} resonance at 40.0 Mc

[b] Reference trifluoroacetic acid

Table 2

ELEMENTAL ANALYSES OF NITROSO RUBBERS

Sample Number	C	H	N	F	O[a]
C_3F_7NO, wt. %	18.10	0.00	7.04	66.82	8.04
XP5675	$18.29 \pm .12$[b]	$0.15 \pm .07$	$6.26 \pm .18$	$61.51 \pm .16$	13.79
XP5702	$18.25 \pm .06$	$0.12 \pm .04$	$6.26 \pm .05$	$66.06 \pm .13$	9.31
XP5812	$18.54 \pm .16$	$0.09 \pm .03$	$6.30 \pm .06$	66.61	8.46
XP5887	$18.54 \pm .04$	$0.06 \pm .01$	$6.38 \pm .00$	67.34	7.68

[a] By difference

[b] Standard deviation

the same as previously reported (Ref. 1) for 3M sample 56703-3.

C. ELEMENTAL ANALYSIS

Both IR and NMR indicate small differences between the four samples submitted. Elemental analyses were conducted to pinpoint these differences. Table 2 itemizes these results.

The theoretical weight percent of fluorine is shown to be 66.82%, and that of hydrogen 0.0%. However, a variation of from 61.5 to 67.3% in fluorine content, and from 0.06 to 0.15% in hydrogen content was indicated by the four samples. It appears that the sample XP5675 may contain a solvent lower in fluorine content than the gum. Further analysis will be necessary to determine the reason for the differences.

D. INTRINSIC VISCOSITY

Some difficulty was experienced in obtaining good viscosity values because of the high gel content of the gums. It was necessary in all cases to filter the .1% solutions through medium frit filters prior to testing. Shown in Figure 6 is the intrinsic viscosity plot for sample XP5702 in FC-43 fluorocarbon at 25°C. Again, using the relationship given by Morneau, Roth, and Schultz (Ref. 2), the weight average molecular weight is found to be about 1.02×10^6, or about three times the Mw of the 3M gum previously tested. Figure 7 shows the intrinsic viscosity plots for sample XP5675 before and after vacuum drying at 80°C for 16 hours. This treatment was found to raise the Mw from 1.12×10^6 to 1.29×10^6, a difference of 170,000, apparently by the volatilization of low molecular weight species.

E. X-RAY DIFFRACTION

All samples were found to be non crystalline, i.e., all gave diffuse diffraction patterns.

F. THERMOGRAVIMETRIC ANALYSIS

Shown in Figure 8 are the thermogravimetric analysis curves for sample XP5675 before and after vacuum drying at 80°C for 16 hours. After this treatment, the TGA curve corresponds to that given by sample XP5702.

G. DIFFERENTIAL THERMAL ANALYSIS

A differential thermal analysis was conducted on sample XP5675 by heating a 50 mg sample in a 4 mm diameter glass tube in a DTA cell

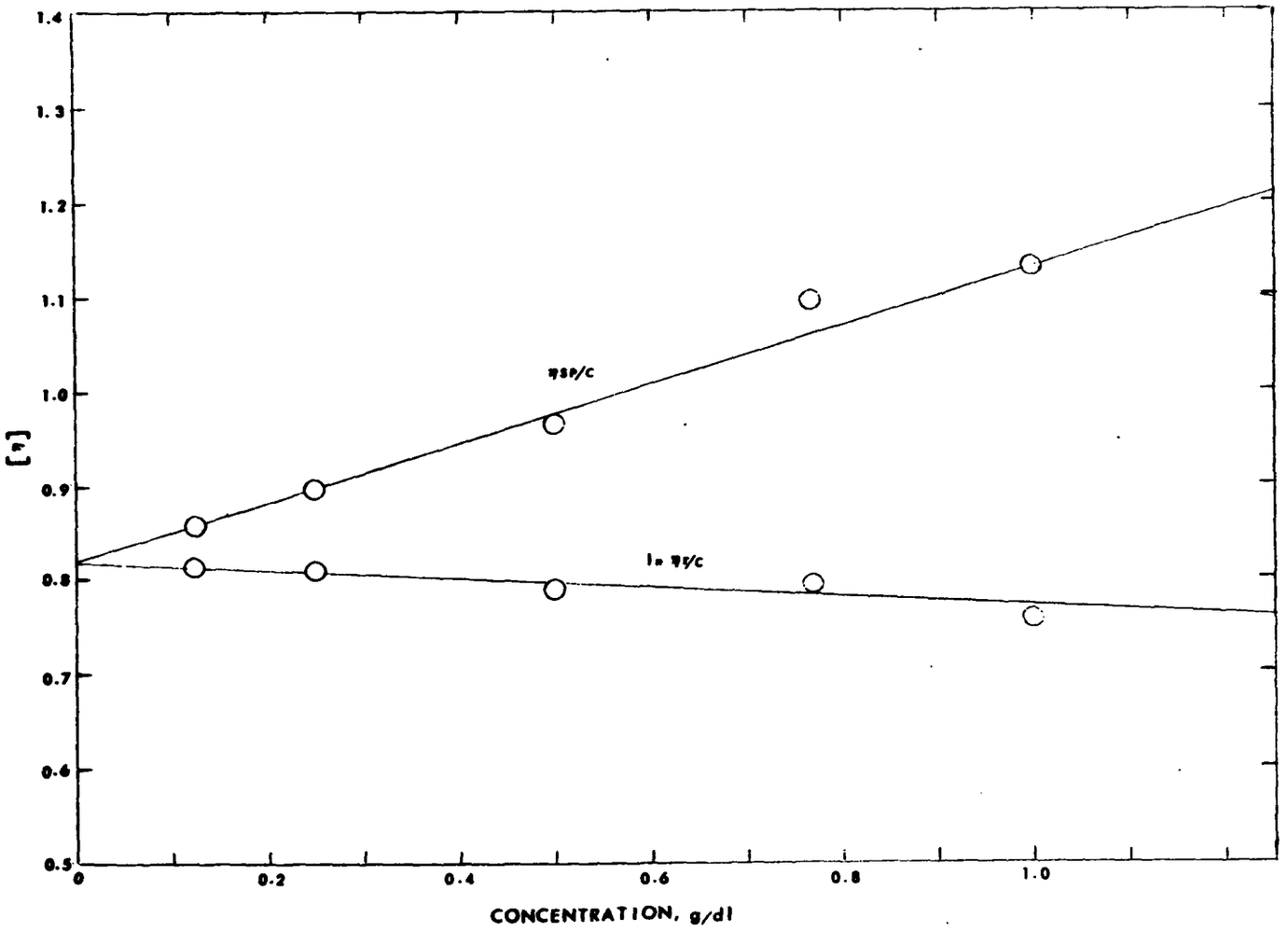


Figure 6. Intrinsic viscosity plot of nitroso rubber sample ZR-561-XP5702 in FC-43 fluorocarbon at 25°C

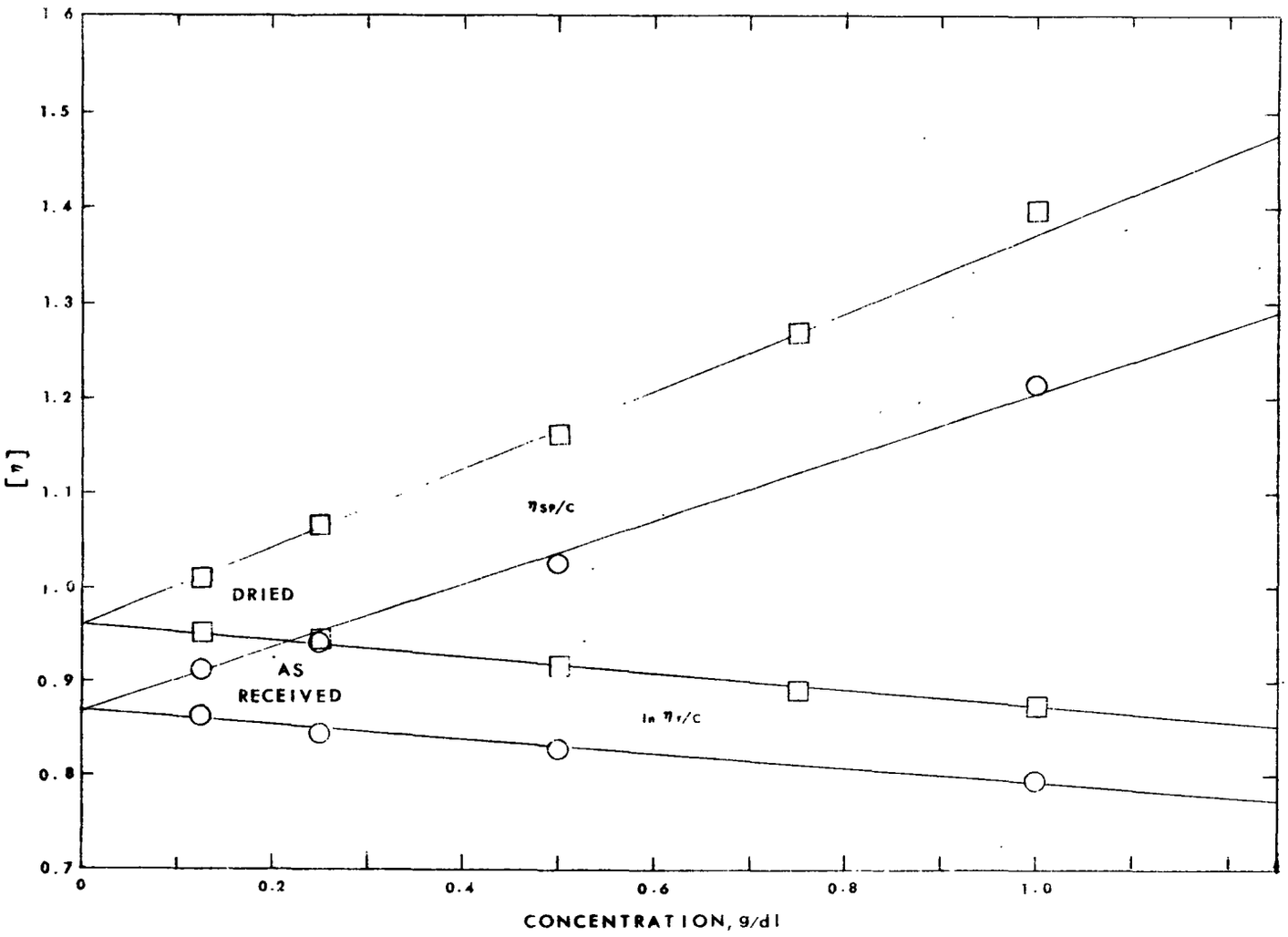


Figure 7. Intrinsic viscosity plot of nitroso rubber sample ZR-561-XP5675 before and after vacuum drying 16 hours at 80°C

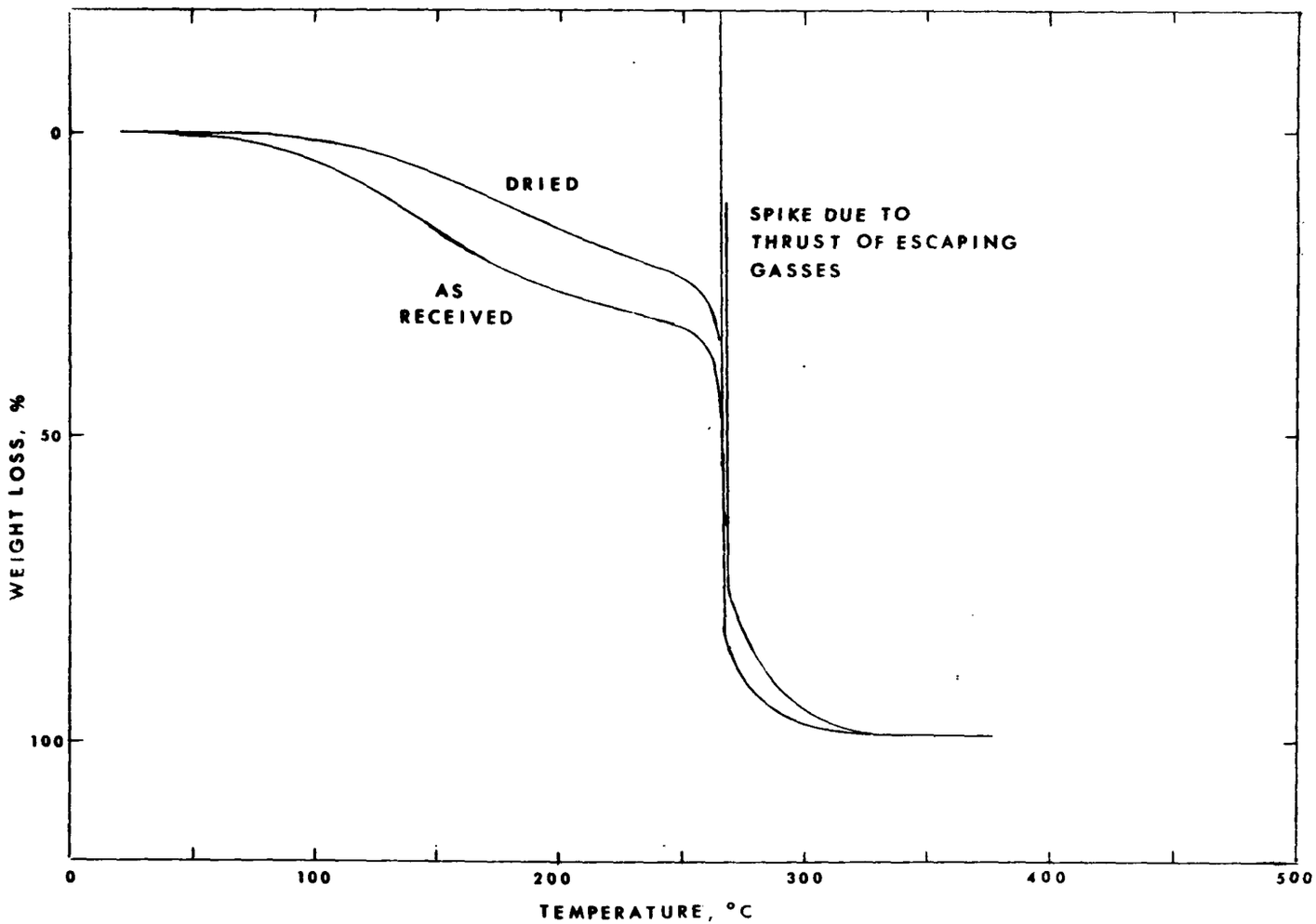


Figure 8. Thermogravimetric analysis curves for nitroso rubber sample ZR-561-XP5675 before and after vacuum drying 16 hours at 80°C

similar to that used in the duPont DTA. The heating rate was 15°C/minute under argon, and the sample was compared thermally to fine alumina powder. At about 250° a mild exotherm became evident, which rapidly gained momentum until by the time 295°C was reached, the exothermic unzipping of the gum was explosive. The sensing thermocouple was blown out of the cell with such force that its impact against the heavy glass envelope of the system cracked the envelope. All precautions are urged in the thermal handling of this material, as a large sample rapidly heated might cause a damaging explosion.

H. CLASH-BERG SHEAR MODULUS

The shear moduli of samples XP5675 and XP5702 as a function of temperature in the Clash-Berg apparatus are shown in Figure 9. The glass transition temperatures, Tg, as approximated by the points of inflection of the curves, are -60° and -45°C, respectively. It should be noted here that sample XP5675, which exhibits an unusually low Tg, also appears to contain a volatile plasticizing agent or solvent, as shown by the TGA curves in Figure 9. The normal Tg for the unplasticized nitroso rubber appears to be about -45°C.

I. REFERENCES

1. Physical and Rheological Properties of Nitroso Rubbers, Quarterly Report No. 4, Contract Nr. DA19-129-AMC-151(N) (O.I. 9115), 24 July 1964.

2. Morneau, G. A., et al., J. Polymer Sci., 55, 609 (1961).

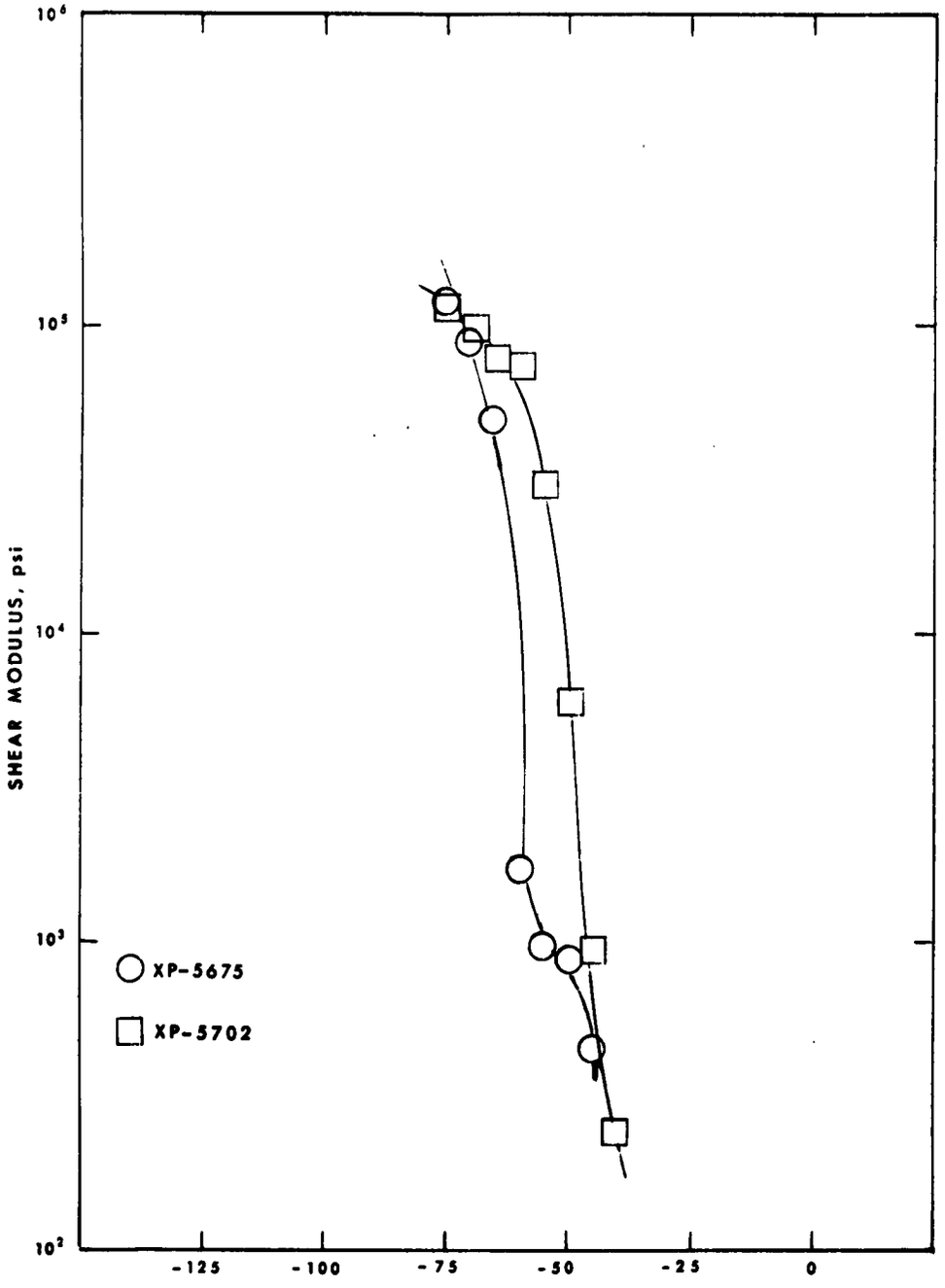


Figure 9. Clash-Berg shear modulus curves for nitroso rubber samples ZR-561-XP5675 and XP5702

III. CONCLUSIONS

Infrared analysis indicated that the four nitroso gums were basically similar to one another and to the 3M-produced gum (9690). Tentative frequency assignments indicate $-CF_2-CF_2-$, and $-CF_2-CF<$ or $>CF-CF<$, the latter two of which do not appear on the idealized average structure obtained by NMR. No $-CF(CH_3)_2$ or $-CF_2CF_3$ was apparent.

Nuclear magnetic resonance defined the structures, as previously reported, to be:

$$\left[\begin{array}{l} N-CF_2CF_2-O \\ | \\ CF_3 \end{array}\right]_x$$

Elemental analysis indicated a variation in fluorine content in the four samples of from 61 to 67%, and hydrogen content from 0.06 to 0.15%. Although unconfirmed, a solvent is believed at fault.

Viscosity measurements were again hindered by high gel content to the extent that accuracy was probably affected by a filtering step. Molecular weights of from 1.0 to 1.3 x 10^6 were determined.

X-ray diffraction on the samples demonstrated noncrystallinity.

Thermogravimetric analysis indicated an initial weight loss at 75°C with a rapid unzipping at 260°C. Vacuum drying of the specimen prior to a run on the TGA decreased the initial weight loss, indicating the volatilization of solvent or low molecular weight material.

Differential thermal analysis exhibited a mild exotherm at 250°C with an EXPLOSIVE exotherm at 295°C. Handling of the nitroso gum at these temperatures should be done with proper SAFETY equipment. The normal Tg for the nitroso rubber tested by the Clash-Berg apparatus is about -45°C.

IV. FUTURE PLANS

The two remaining supplied samples will receive characterization deemed significant in light of the results of the four tested samples.

Further characterization, including molecular weight distribution and average molecular weight, density, coefficient of thermal expansion, second-order transition by shear modulus, and the calibration of molecular weight to the intrinsic viscosity of solvents other than FC-43 will be conducted using the six samples. The extent of impurities such as solvent or nonreacted monomer will be determined.

V. TIME AND FINANCIAL STATUS

	Hours (to 12/31)
Lucius Gilman*, Manager, Plastics and Polymer Research	130
George L. Ball III, Research Physicist	536
Ival O. Salyer, Research Manager	27
Harry S. Wilson, Research Group Leader	140
John V. Pustinger, Analytical Group Leader	9
William R. Smith, Analytical Chemist	5
Professional	847
Rodrigue G. Thibodeau, Research Technician	238
Charlotte S. Fritsch, Research Technician	259
John E. Strobel, Research Technician	17
Richard L. Evers, Research Technician	24
Conrad A. Cenerizio, Research Technician	26
Margaret S. Ross, Research Technician	16
Technical	580
Grand Total	1427

* Project Leader

$19,051 has been spent as of 31 December 1964. The contract is for $59,335, leaving a balance of $40,284.

34% of work has been completed and 32% of the money spent. The money remaining on the contract is sufficient. However, a 10-month extension in time will be necessary to complete the work.

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Security Classification

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Ball, George L. III, Salyer, I. O., Wilson, H.S.

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c	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*: None
d.	

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Available through sponsoring agency only.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
None	U. S. Army Natick Laboratories Natick, Massachusetts

13. ABSTRACT

Four nitroso gum samples produced by Thiokol Chemical Corporation and supplied by the U. S. Army, Natick, Massachusetts, were characterized by IR, NMR, elemental analysis, intrinsic viscosity, X-ray diffraction, TGA, DTA and Clash-Berg shear modulus. Infrared analyses indicated that the four gums were basically similar. NMR confirmed a previously reported tructure of $\left[N\text{-}CF_2CF_2\text{-}O\right]_x$ (CF_3). Elemental Analysis, however, indicated a variation in fluorine content from 61 to 67%. Molecular weights by intrinsic viscosity were in the range of 1.0 to 1.3 x 10^6. TGA confirmed a previously disclosed weight loss at 75°C with unzipping at 260°C. DTA exhibited a mild exotherm at 250°C with an EXPLOSIVE exotherm at 295°C. Glass transitions of -60°C and -45°C were found by means of the Clash-Berg shear modulus apparatus. However, it was felt that the -60°C transition may be due in part to the presence of solvent.

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